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ARTICLE

RESEARCH PROGRESS IN CO PYROLYSIS OF BIOMASS AND WASTE PLASTICS

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ABSTRACT

This paper briefly introduces recent progress in biomass pyrolysis, waste plastic pyrolysis, and co-pyrolysis of biomass and waste plastic. The potential of China for co-pyrolysis of biomass and waste plastic is estimated in recent years. A development strategy for the co-pyrolysis of biomass and waste plastic is proposed.

KEYWORDS

Biomass, Waste Plastic, Co-Pyrolysis

1. INTRODUCTION

Plastic and its products have become indispensable substances in people's daily life. According to statistics, 3.6 million tons of plastics are produced and put into the market every year in China, and about 2.5 million tons of waste plastics are generated, and the recycling rate of waste plastics is less than 20% [1]. These waste plastics cause serious "white pollution", which not only pollutes the environment but also greatly wastes resources. Therefore, how to deal with and dispose of a large number of waste plastics has become an urgent problem to be solved in environmental governance.

Most of today's various energy and chemical raw materials come from fossil resources. In the process of utilization of fossil raw materials, it will inevitably bring about environmental pollution problems such as a net increase in atmospheric carbon dioxide concentration and continuous reduction of fossil resources, resulting in resource depletion and pollutant emissions. Therefore, it is urgent to develop renewable and recyclable new energy and chemical raw materials, and at the same time reduce the emission of pollutants as much as possible. In the 21st century, human beings will face severe challenges of energy and environmental issues. The development and utilization of renewable energy and the reduction of pollutant emissions are major issues related to the sustainable development of the national economy, national security, and social progress. According to the "Notice of the State Council on Printing and Distributing Comprehensive Work Plans for Energy Conservation and Emission Reduction", the current situation is very severe to achieve energy conservation and emission reduction targets. Last year, the country failed to achieve the goals of energy conservation and pollution reduction set at the beginning of the year, which made it more difficult to work on energy conservation and emission reduction in the next four years. Therefore, converting biomass and waste into energy is an important action to prevent global warming and develop energy resources.

This paper mainly introduces the research progress of biomass, waste plastic, biomass, and waste plastic co-pyrolysis, and summarizes the utilization status, potential, and future development direction of such renewable resources.

2. RESEARCH STATUS OF BIOMASS PYROLYSIS AT HOME AND ABROAD

During the oil crisis in the 1970s, countries all over the world sought renewable energy that can replace fossil energy, and "biomass" gradually attracted people's attention, so biomass research began, especially the research on biomass pyrolysis. It has attracted the attention of many researchers.

There are two types of pyrolysis of biomass: slow cracking and flashing. Biomass is pyrolyzed into slow cracking at a slow heating rate (5-7 K/min). In this way, fewer liquid and gaseous products are obtained from pyrolysis, and the yield of coke is greater. Researchers have made a series of meaningful reports on the slow pyrolysis of biomass. Ozbay et al. [2] reported the slow cracking of cottonseed at a heating rate of 7 °C/min in two tubular reactors. The results showed that before 600 °C, the oil yield increased with the increase of the pyrolysis temperature, but when heated to 750 °C, the oil yield decreased. The yield of coke continued to decrease. The maximum oil yield was obtained when the nitrogen flow rate was 100 cm3/min. Onay and Kockar [3] conducted experiments on the slow cracking of rapeseed at different temperatures, different nitrogen flow rates, and different particle sizes. They found that oil yield increased with increasing temperature up to 550°C, and then decreased with increasing temperature. The coke yield decreased and the gas yield increased with increasing temperature. When the particle size is within the range of $0.6<dp<0.85$, the oil yield reaches the highest level. While the particle size is within the range of $0.85<dp<1.25$, the coke content is the least. Beis et al. [4] used a fixed bed slow cracking experiment to crack safflower seeds at a heating rate of 5 °C/min. The pyrolysis temperature, gas flow rate, particle size, and other conditions were changed during the experiment, and it was found that within the tested particle size and gas flow rate range, the oil yield was the highest at 550 °C, and the gas yield was the highest at 700 °C. In all experiments performed, the coke yield decreased with increasing temperature.

Most of the initial studies on biomass pyrolysis used slow pyrolysis, and the disadvantage of this pyrolysis is that the content of coke produced is relatively high. However, what is desired from the pyrolysis of biomass is a high yield of liquid products, which requires the use of flashing methods. Flashing requires a reaction time of only a few seconds or less, so the heating rate is very high, typically 300°C/min. And in general, flashing can obtain high-quality bio-oil. In recent years, the flashing has been successfully used in many fluidized bed reactors because the fluidized bed reactor has the advantages of a high heating rate, rapid separation of volatiles, easy control, and easy product collection [5], and many countries have carried out a large number of studies on the biomass pyrolysis reactor [6-16].

The pyrolysis process of biomass is affected by various factors. Onay et al. [17] used a fixed-bed reactor to study the flash decomposition of rapeseed. Under the conditions of a pyrolysis temperature of 550 °C, a particle size of 0.6-0.85 mm, a heating rate of 300 °C/min, and a nitrogen flow rate of 100 cm3/min, the yield of oil obtained by pyrolysis was 68%. Onay and Kockar [18] studied the effect of pyrolysis temperature, heating rate, particle size, and gas flow rate on the flashover of rapeseed. It was found that the coke yield decreased from 27% to 14.5% with increasing temperature. Under the conditions of a temperature between 550 and 600℃, particle size between 0.6mm and1.25mm, and a gas flow rate of 100cm3/min, the maximum yield of oil obtained by pyrolysis was 73%.

Biomass rapid pyrolysis technology is an important way of biomass utilization, and many researchers use flashing to increase the liquid and gas products of pyrolysis. Horne and Williams [19] used a fluidized bed reactor to flash waste wood. The reaction was carried out under the temperature of 400 °C, 500 °C, and 550 °C respectively, and the liquid and gaseous products increased while the coke content decreased with increasing temperature. Scott and Piskorz [20] reported the flashover of aspen under different experimental conditions. The experimental results of flashing of maple, aspen, and wheat straw showed that with the increase of temperature, the liquid and gas products increased, while the coke content decreased [21].

Zhejiang University [22] pyrolyzed rosewood in a fluidized bed. It was found that the yield of coke decreased gradually with the increase in temperature and stabilized to a constant value. The yield of pyrolysis oil is the largest when the temperature is between 500℃ and 550℃. If the reaction temperature is too low, the biomass cracking may be incomplete, and if the temperature is too high, the gas yield will increase.

Biomass pyrolysis products, especially liquid products, are good substitutes for depleted fossil fuels. The method of thermochemical transformation is the most suitable method to obtain the desired substitute product. The quality of the products obtained by pyrolysis is better than that obtained by any other thermochemical method. The residues of deforestation and wood processing and agricultural and forestry residues such as straw, wheat straw, and other raw materials are pyrolyzed to make them high-grade energy, improving the thermal efficiency of use, and reducing the use of fossil energy. That is an inevitable trend to protect the environment and promote sustainable development.

3. RESEARCH STATUS OF WASTE PLASTIC PYROLYSIS AT HOME AND ABROAD

To overcome the shortcomings of waste plastic recycling and incineration, researchers have turned their attention to converting waste plastics into valuable liquid or gaseous fuels and activated carbon monomers. The method used is pyrolysis, that is, the waste plastics are heated and decomposed under inert gas, and their original structure is destroyed to generate value-added oligomer products, which can be used as fuel or raw materials for some petrochemical industries. The resulting vapor and liquid phase products are mixtures of hydrocarbons and other organic compounds, the composition of which depends on the composition of the waste plastic. It can be seen that pyrolysis of waste plastics is an important waste-to-treasure treatment method to convert waste plastics into hydrocarbons with economic value.

Pinto [23] et al. studied the effect of waste plastic components on pyrolysis products. Typical waste plastics contain 68% polyethylene, 16% polypropylene, and 16% polystyrene. The experimental results show that the final pyrolysis product depends on the components of the waste plastic. The presence of polyethylene increases the alkane content. The content of polystyrene pyrolysis aromatic hydrocarbons is relatively high. Polypropylene pyrolysis is relatively easy to generate olefinic compounds. The mixed pyrolysis of polystyrene and polypropylene increases the content of octane in the final product, from which it can be seen that the desired pyrolysis product can be obtained by properly mixing and pyrolyzing waste plastics. The pyrolysis of waste polyethylene and waste polystyrene was reported by Kiran and Demirbas et al. The experimental results show that more liquid products are obtained from waste polystyrene, while more gaseous products are obtained from waste polyethylene. The main liquid product of waste polystyrene is styrene monomer, in addition to 37% of toluene, naphthalene, and xylene. The main pyrolysis products of waste polyethylene are biphenyl compounds. By comparing the high-value aromatic compounds obtained by pyrolysis, it was found that the aromatic compounds obtained from waste polystyrene were higher than that of waste polyethylene, and the aromatic compounds accounted for 63% of the entire fuel oil product obtained by pyrolysis. Nilgun KiranCiliza et al. reported the pyrolysis of waste polypropylene and pure polypropylene and mixtures of waste polypropylene and polyethylene and polystyrene under slow conditions. They studied not only the effect of waste on pyrolysis products but also the effect of mixture ratios on pyrolysis products. The liquid products obtained in the experiment include aliphatic, aromatic, and polyaromatic, and the yield increases with the increase of polypropylene content in the waste plastic mixture. The proportions of olefins and alkanes in the gas phase product also vary with the proportions of different substances in the waste plastic. Kyong-Hwan Lee et al. reported the characteristics of liquid products obtained by pyrolysis of waste plastic mixtures at low temperatures and high temperatures and discussed the effect of reaction decay time on liquid products.

Domestic pyrolysis of waste plastics mainly focuses on the research on waste plastics' pyrolysis temperature, pyrolysis characteristics, weight loss rate, pyrolysis products, and catalytic pyrolysis [28,29]. The pyrolysis reaction of various waste plastics shows that the temperature of the pyrolysis reaction of various plastics is different. Polyethylene decomposes at 280°C. Polypropylene begins to decompose at around 300°C and terminates at around 350°C. Polystyrene can be pyrolyzed at about 400 °C to obtain crude styrene monomer. The pyrolysis characteristics of waste polystyrene show that waste polystyrene can be pyrolyzed into styrene-based pyrolysis products, and the liquid product reaches 96%, of which the styrene content is more than 70%, which are mainly benzene, toluene, ethylbenzene, styrene, etc. For polyethylene and polypropylene, as the pyrolysis temperature increases, the gas yield increases, the content of pyrolysis products with high carbon numbers (from C21 to C30) decreases, and the content of light components (from C3 to C4) increases relatively.

4. RESEARCH STATUS OF CO-PYROLYSIS OF BIOMASS AND WASTE PLASTICS AT HOME AND ABROAD

There are some reports on biomass and coal research. However, research on the co-pyrolysis of biomass and waste plastics is rarely reported even in foreign countries. The co-pyrolysis of biomass and medium-density polyethylene and polypropylene mixtures was studied by Sharypov et al. in Russia. Initial thermogravimetric experiments showed that the temperature of biomass pyrolysis was lower than that of polyolefins, indicating that the mixture of biomass and plastics has independent thermal behavior. Through experiments, it is concluded that the optimum temperature for the co-pyrolysis of biomass and plastic to obtain the light liquid product with the maximum yield is 400 °C; when the mass mixing ratio of biomass and plastic is less than 1:1, the light liquid product obtained is obtained. It is greater than the weight of the two separate pyrolyzes; when the mass mixing ratio of biomass and plastic is 20:80, the maximum light liquid product is about 40%, which is more than twice the weight of light liquid products obtained by pyrolysis of biomass and plastic alone; only 8% (volume fraction) of unsaturated hydrocarbons were detected in the resulting gas product, while the gas products of the pyrolysis plastic alone contained 75% olefins. Sharypov et al. further studied the heavy liquid phase products obtained by co-pyrolysis of biomass and plastics in a mass ratio of 1:1

using the Fourier transform red light spectroscopy, nuclear magnetic resonance, gas chromatography/mass spectrometry, and other techniques. The results show that the average molecular weight of the heavy liquid phase product obtained by co-pyrolysis of biomass and plastic is smaller than that of the heavy liquid phase product obtained by pyrolysis of plastic alone. The molecular weight of the liquid phase product obtained by the mixed co-pyrolysis of polypropylene plastic and biomass ranges from 230 to 250, and the molecular weight of the liquid phase product obtained by the mixed co-pyrolysis of polyethylene plastic and biomass ranges from 480 to 540. The relative molecular mass of the obtained heavy liquid phase product is more than 1.5 to 2.5 times that of mixed pyrolysis. Marin et al. mainly studied the liquid phase products obtained by co-pyrolysis of biomass and polyolefins in a mass ratio of 1:1, and the yield was over 50%. Through analysis and characterization, it was known that the light liquid phase products only contained olefins, alkanes, and some aromatic hydrocarbons (benzene, toluene, and xylene). These substances are mainly derived from polyolefins, 2-enes containing 3n carbon atoms are mainly derived from biomass, and more than 80% of the heavy liquid phase products are macromolecules olefins and paraffin. The research on the co-pyrolysis of biomass and polyolefin mixture by Jakab and Matsuzawa showed that the biomass has been completely pyrolyzed under the experimental conditions of 400 °C, and the thermogravimetric analysis of biomass and biomass and plastic mixture was clear. Thermogravimetric analysis of biomass and the mixture of biomass and plastic showed clearly that the pyrolysis of biomass was independent, and the pyrolysis loss occurred below 400°C. Moreover, these studies have shown that the co-pyrolysis of biomass and waste plastics has obvious synergistic effects, which indicates that the co-pyrolysis reaction has potential application prospects.

Co-pyrolysis of biomass and polyolefin macromolecules increased light liquid phase products and 2-olefins. Studies have shown that when the biomass content accounts for 20%, the obtained light liquid phase products have the highest content [34]. However, the liquid phase obtained by co-pyrolysis contains a large number of olefinic hydrocarbons [35], which essentially limit the direct utilization of valuable products such as engine fuels and organic solvents. Sharypov et al. further reported the catalytic co-pyrolysis of biomass and polyolefin polymers in a hydrogen atmosphere. The study found that the optimal temperature of co-pyrolysis was 400°C, and at this temperature, the number of liquid-phase products obtained from the co-pyrolysis reaction was the largest. The yields of liquid-phase products ranged from 14 to 19 wt%. After adding catalysts such as hematite and pyrite, the yield of liquid phase products increased by 14% to 21% by weight, and the content of olefins and naphthenes decreased by about 2 to 3 times.

It can be seen from the above content that the research on the co-pyrolysis of biomass and plastics is only carried out by the research group headed by Sharypov of Russia, and other countries have not seen relevant reports.

There are relatively few studies on the co-pyrolysis of biomass and waste plastics in China. Deng Daiju of Sichuan University et al. made a self-made fixed-bed reactor to study the co-pyrolysis of propylene and bamboo, and the influences of reaction atmosphere, pyrolysis temperature, reactant ratio, and reaction time on co-pyrolysis were discussed. The experimental results show that the mutual influence of Moso bamboo and polypropylene in the pyrolysis process, the liquid yield and product distribution of the two co-pyrolysis are different from those of the two separate pyrolyzes, and the octane number of the oil phase liquid product varies with Moso bamboo. It increases with the increase of the added amount. Under the optimal ratio of polypropylene and bamboo, the synergistic effect of the two co-pyrolysis is the most obvious, not only the conversion rate of the raw material is the largest, but also the yield of the obtained liquid product is the highest, and the hydrogen atmosphere is relatively high. The nitrogen atmosphere is more conducive to the formation of oil phase products and the pyrolysis of lignin components in Phyllostachys pubescent. And the conditions for obtaining the best oil phase liquid yield are as follows. The ratio of polypropylene and Moso bamboo is 8:2, the pyrolysis temperature is 520°C, the reaction time is 4h, the hydrogen atmosphere, the oil phase liquid yield is 53.9wt%, and the octane number is 53.9%. is 77.3.

5. DEVELOPMENT POTENTIAL OF CO-PYROLYSIS OF BIOMASS AND WASTE PLASTICS IN CHINA

Biomass is the only renewable green energy, which includes animals, plants, and microorganisms as well as all organic substances excreted and metabolized by these living organisms. As the carrier of biomass energy, biomass is unique among various renewable energy sources. It not only can store solar energy but also is a renewable carbon source that can be converted into conventional solid, liquid, and gaseous fuels. More importantly, the sustainable use of biomass will not increase the net emission of carbon dioxide, so the global climate will benefit from the extensive application of biomass, which meets the requirements of energy demand and environmental protection. Biomass thermal cracking is currently the most efficient type of energy conversion process. Because it can generate pyrolysis oil intermediates, which can then be refined to generate higher-value chemicals and energy carriers. China is rich in biomass resources, mainly agricultural and forestry waste, agricultural and forestry energy plants, organic waste and waste, and biomass waste oil. The annual total available amount exceeds 1 billion tons, which can meet the raw material supply of the multi-structured biomass liquid fuel production of 100 million tons per year. It can be seen that the potential resources of biomass energy in China are very large, and the use of modern biomass technology to develop biomass energy is of great significance and has a very broad prospect. Moreover, the active development of biomass energy will help to solve the "three rural problems", and can also effectively alleviate the environmental pressure, and realize the energy strategy, agricultural income increase, environmental protection, and other issues. In particular, China has just started in the effective utilization of biomass resources, and its technology and theoretical research are far behind developed countries. Therefore, it is urgent to increase the research on the development and utilization of this energy. Both sustainable development and environmental protection are of great importance.

The development of the plastics industry has played a huge role in the development of other industries and the improvement of people's living standards. However, as people pay more and more attention to the living environment, we have to consider the recycling and reuse of the aftermath. Improper handling can bring unexpected negative impacts on the environment. The disposal and recycling of waste plastics have attracted people's attention as a social and economic issue at the same time. Statistics show that the total amount of plastic waste in the world has reached 4.46 million tons, and China's is about 1.6 million tons. The recycling rate is extremely low, so it has a broad prospect for further development. The production of pyrolysis fuels or high-value-added products from waste plastics plays an important role in protecting the environment and preventing pollution and harm to the ecosystem. However, waste plastics have poor thermal conductivity and high melt viscosity. Pyrolysis alone can easily lead to coking, and there are many heavy liquid phase products obtained from pyrolysis, which is difficult to directly use as fuel oil.

However, co-pyrolysis of biomass and waste plastics in a suitable ratio can reduce the relative molecular weight of liquid products, improve the yield of light liquid products, and reduce the oxygen content of heavy liquid products, and the olefins in gas products. material is significantly reduced. Co-pyrolysis of biomass and waste plastics can not only solve the shortcomings of separate pyrolysis of biomass and waste plastics but also make full use of waste resources. Therefore, according to Chinese current national conditions, biomass and waste plastics are co-heated decomposition of fuel or high value-added products has strong practical significance and broad development potential.

6. DEVELOPMENT STRATEGY OF CO-PYROLYSIS OF BIOMASS AND WASTE PLASTICS

China is a big agricultural country with abundant biomass resources. The annual output of non-wood fibers such as straw, wheat straw, bagasse, reed, and bamboo alone exceed 1 billion tons. These non-wood fibers and a large amount of wood processing residues are inexhaustible natural polymer chemical raw material warehouses and energy. However, at present, 3 billion tons of straw are not used effectively every year, most of them are burned in vain, and there are also many forest wastes. Due to the low dispersion and low energy density of biomass energy distribution, it is very difficult to utilize. The utilization rate of these bio-energy sources is only 10% to 20%. Therefore, it is imperative to strengthen our country's research in this area.

The rational development and use of waste plastic resources can not only bring good economic benefits, but also solve environmental problems. However, the recycling rate of waste plastics in China is not high, and there is a clear gap with developed countries. Most of the existing processes use a single variety of processing waste or polyolefin waste plastics as raw materials, and the processes and equipment used are mostly those of the petroleum cracking process, which lack comprehensive consideration of the characteristics of the waste plastic cracking reaction.

Overall, the development and utilization of biomass and waste plastics in China is still in the early stage of development, and there are still many problems, mainly including unclear resources, immature technology, and imperfect policies and markets. In view of the research status of biomass and waste plastics, especially the current domestic and foreign research, there are relatively few studies on the co-pyrolysis of biomass and waste plastics, and this field has just begun to be involved in China. Therefore, the research on the co-pyrolysis of biomass and waste plastics should be strengthened in the future, and the synergy of the co-pyrolysis of biomass and waste plastics should be further studied. The mechanism of action has achieved a breakthrough in co-pyrolysis technology. At the same time, to realize the direct use of pyrolysis oil as fuel, the research and exploration of the application of catalysts in the co-pyrolysis of biomass and polymers should be strengthened in the future, and the development of co-heating technology of biomass and waste plastics in my country should be vigorously promoted.

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